

Diaquabis(1*H*-imidazole- κ N³)bis(4-nitrobenzoato- κ O¹)cadmium

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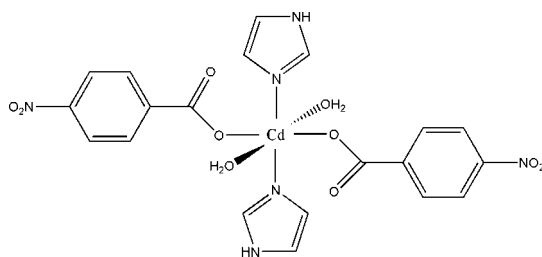
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.026; wR factor = 0.076; data-to-parameter ratio = 15.0.

In the centrosymmetric title compound, $[\text{Cd}(\text{C}_7\text{H}_4\text{NO}_4)_2 \cdot (\text{C}_3\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2]$, the Cd^{II} atom, located on an inversion center, is coordinated by two N atoms and four O atoms in an octahedral geometry. The internal cohesion of the molecule is enhanced by an intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond. Intermolecular $\text{O}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds and $\pi-\pi$ contacts [centroid-centroid distance = $3.6549(2)$ Å] define two-dimensional networks parallel to (001), which are further connected by weaker $\text{C}-\text{H} \cdots \text{O}$ interactions into a weakly connected three-dimensional supramolecular framework.

Related literature

For general background to aromatic carboxyl acid complexes, see: Kuang *et al.* (2007); Hsu *et al.* (2011). For related structures, see: Zheng *et al.* (2008).



Experimental

Crystal data

$[\text{Cd}(\text{C}_7\text{H}_4\text{NO}_4)_2 \cdot (\text{C}_3\text{H}_4\text{N}_2)_2(\text{H}_2\text{O})_2]$
 $M_r = 614.80$
Triclinic, $P\bar{1}$

$a = 5.8017(12)$ Å
 $b = 8.0253(16)$ Å
 $c = 12.879(3)$ Å

$\alpha = 77.99(3)^\circ$
 $\beta = 88.42(3)^\circ$
 $\gamma = 85.16(3)^\circ$
 $V = 584.4(2)$ Å³
 $Z = 1$

Mo $K\alpha$ radiation
 $\mu = 1.00$ mm⁻¹
 $T = 293$ K
 $0.33 \times 0.14 \times 0.09$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.989$, $T_{\max} = 0.989$

5719 measured reflections
2627 independent reflections
2511 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.076$
 $S = 1.24$
2627 reflections
175 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.54$ e Å⁻³
 $\Delta\rho_{\min} = -0.80$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O5}-\text{H5A} \cdots \text{O2}$	0.84 (1)	1.88 (1)	2.679 (1)	159
$\text{O5}-\text{H5B} \cdots \text{O1}^{\text{i}}$	0.84 (1)	1.97 (1)	2.785 (1)	164
$\text{C2}-\text{H2A} \cdots \text{O5}^{\text{ii}}$	0.93	2.58	3.244 (1)	129
$\text{C3}-\text{H3A} \cdots \text{O5}^{\text{iii}}$	0.93	2.43	3.344 (1)	169
$\text{C10}-\text{H10A} \cdots \text{O2}$	0.93	2.42	2.751 (4)	101

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y - 1, z$; (iii) $-x, -y + 2, -z$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2473).

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supplementary materials

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Diaquabis(1*H*-imidazole- κ N³)bis(4-nitrobenzoato- κ O¹)cadmium

Yan-Li Mao, Xiao-Ke Yu and Jian-Li Lin

Comment

Aromatic carboxyl acid complexes have been paid great attention these years for their potential applications in gas storage, separation, catalysis, magnetism, luminescence, and drug delivery (Kuang *et al.*, 2007). As a N-containing aromatic carboxyl acid, nitrobenzoic acid has been widely used in dye intermediate, organic synthesis, sensitization material, functional pigment (Hsu *et al.*, 2011). So far, to our knowledge, cadmium complexes constructed from 4-nitrobenzoato and imidazole have not been reported. In order to get new Cd^{II} complexes with novel functions and discover their structure-property relationship, a new complex [Cd(C₇H₄NO₄)(C₃H₄N₂)(H₂O)] was synthesized.

The asymmetric unit of [Cd(C₇H₄NO₄)(C₃H₄N₂)(H₂O)] consists of a Cd²⁺ ion lying on an inversion centre, a 4-NBA⁻ ion (4-HNBA = 4-nitrobenzoic acid), one imidazole ligand and one lattice water as illustrated in Fig. 1. The Cd²⁺ cation is octahedrally coordinated by two N atoms of imidazole ligands, two O atoms from two 4-NBA⁻ ions and two O atoms from two lattice water molecules; it takes a (4 + 2) octahedral geometry, with the oxygen atoms located in the equatorial plane (Cd—O1 = 2.364 (2) Å, Cd—O5 = 2.367 (2) Å, and the two nitrogen atoms occupying the axial position (Cd—N1 = 2.255 (2) Å). Table 1 presents the \cdots contact information involving the C₃N₂ ring (centroid, Cg1) and Table 2, the more meaningful H-bonds in the structure; the most important ones are those involving water H's. The one described in the first entry in Table 2 is intramolecular; the second one, instead defines chains along *a* (Figure 2, vertical arrays). The weak one involving C2—H2A (Table 2, third entry) and the π – π contact (Table 1) link chains into a two-dimensional supramolecular network parallel to (001) as illustrated in Figure 2. Finally, the remaining weak H-bonds link these 2D structures into a 3D supramolecular architecture (Figure 3).

Experimental

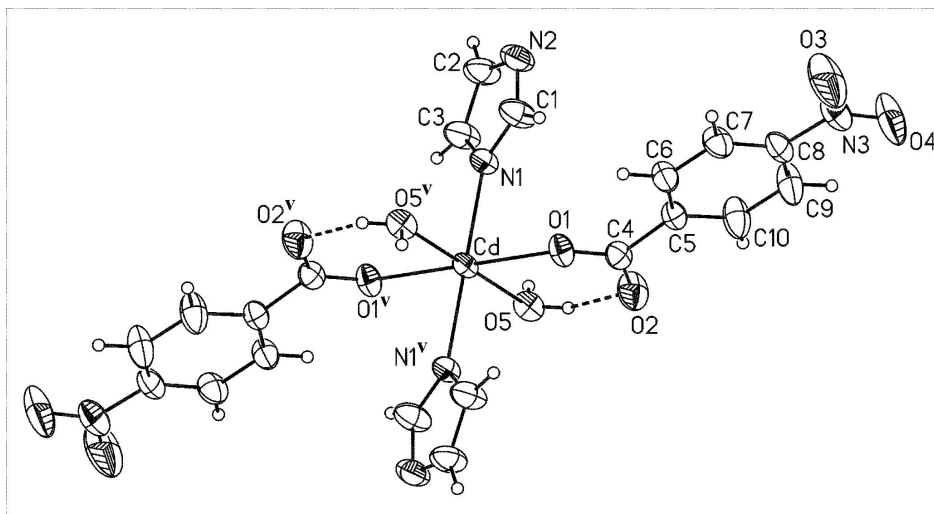
Dropwise addition of 1.0 ml (1 *M*) of K₂CO₃ to a stirred aqueous solution of Cd(CH₃COO)₂·2H₂O (0.266 g, 1.0 mmol) in 10.0 ml of H₂O yielded a fine white precipitate, which was separated by centrifugation and washed with water until no CH₃COO⁻ anions were detectable in the supernatant. The fresh precipitate was then added to a stirred aqueous solution of 4-nitrobenzoic acid (0.167 g, 1.0 mmol) in C₂H₅OH/H₂O (1:1, 20.0 ml), producing a white suspension, to which imidazole (0.137 g, 2.0 mmol) was added. The mixture was further stirred vigorously for about 0.5 h. After filtration, the white filtrate (pH = 6.59) was maintained at room temperature and colorless crystals were grown.

Refinement

H atoms bonded to C atoms were placed in geometrically calculated positions and were refined using a riding model. H atoms attached to O atoms were found in a difference Fourier synthesis and were refined with restrained O—H = 0.84 (1) Å. In all cases, *U*_{iso}(H) values were set at 1.2 *U*_{eq}(host).

Computing details

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

**Figure 1**

ORTEP view of the title compound, The displacement ellipsoids are drawn at 45% probability displacement ellipsoids. Symmetry code: (v) 1-x, 2-y, -z.

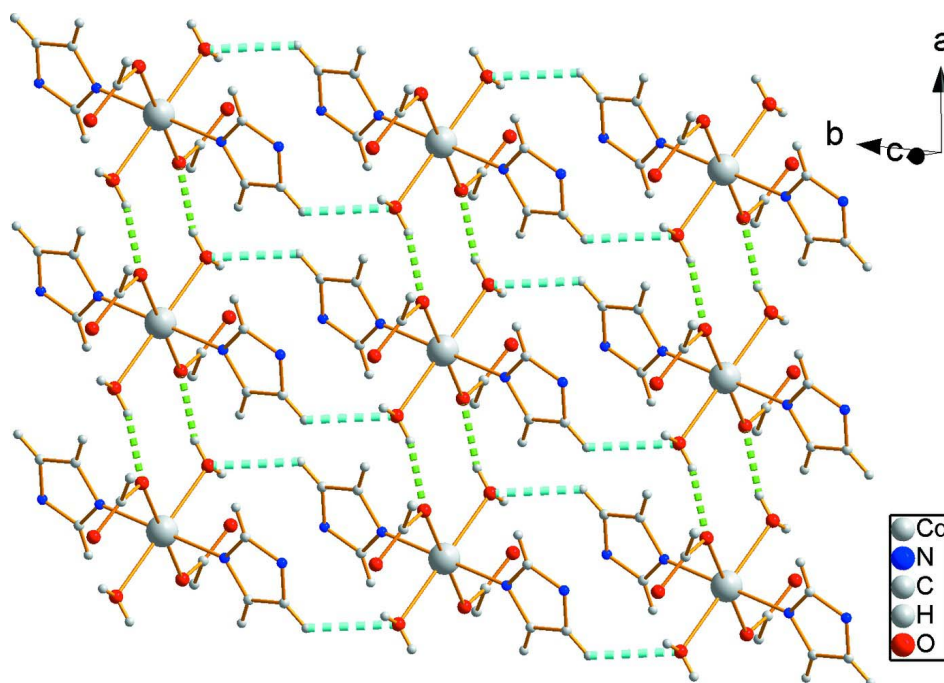


Figure 2

The two-dimensional supramolecular networks parallel to (001). In order to observe how the complex molecules form two-dimensional layers clearly, nitrobenzene on 4-nitrobenzoato molecules which are not engaged in link the components into a two-dimensional layers were omitted.

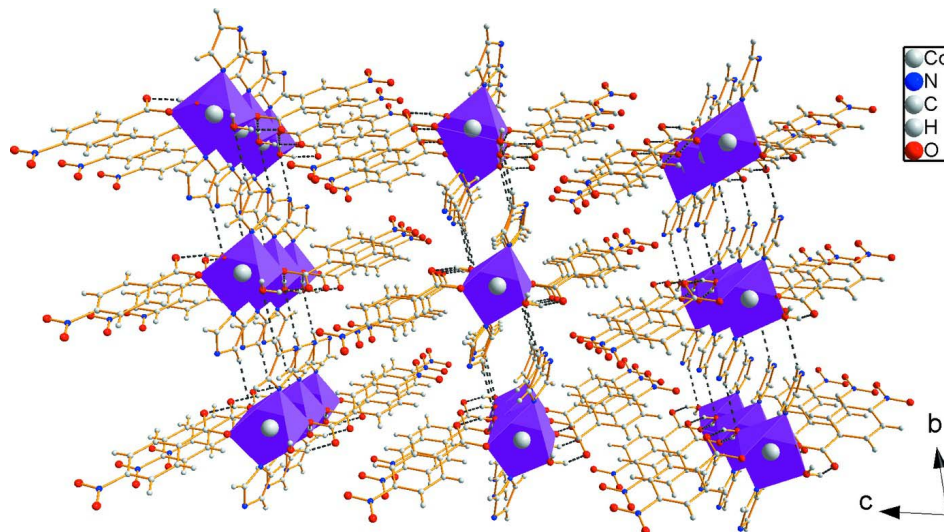


Figure 3

The three-dimensional framework of title complex.

Diaquabis(1*H*-imidazole- κN^3)bis(4-nitrobenzoato- κO^1)cadmium

Crystal data

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 $M_r = 614.80$

Triclinic, $P\bar{1}$
Hall symbol: -P 1

$a = 5.8017(12) \text{ \AA}$
 $b = 8.0253(16) \text{ \AA}$
 $c = 12.879(3) \text{ \AA}$
 $\alpha = 77.99(3)^\circ$
 $\beta = 88.42(3)^\circ$
 $\gamma = 85.16(3)^\circ$
 $V = 584.4(2) \text{ \AA}^3$
 $Z = 1$
 $F(000) = 308$

Data collection

Rigaku R-Axis RAPID
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)
 $T_{\min} = 0.989$, $T_{\max} = 0.989$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.076$
 $S = 1.24$
2627 reflections
175 parameters
3 restraints
Primary atom site location: structure-invariant
direct methods

$D_x = 1.747 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Cell parameters from 5719 reflections
 $\theta = 3.2\text{--}27.5^\circ$
 $\mu = 1.00 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
Plate, colorless
 $0.33 \times 0.14 \times 0.09 \text{ mm}$

5719 measured reflections
2627 independent reflections
2511 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -6 \rightarrow 7$
 $k = -10 \rightarrow 10$
 $l = -16 \rightarrow 16$

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.3927P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.80 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd	0.5000	1.0000	0.0000	0.03040 (10)
N1	0.4161 (4)	0.7310 (3)	0.07261 (18)	0.0351 (5)
C1	0.5412 (6)	0.6131 (4)	0.1376 (3)	0.0497 (8)
H1A	0.6844	0.6290	0.1632	0.060*
C2	0.2360 (6)	0.4946 (4)	0.1116 (3)	0.0518 (8)
H2A	0.1261	0.4160	0.1136	0.062*
N2	0.4388 (5)	0.4676 (3)	0.1627 (2)	0.0500 (7)
C3	0.2227 (6)	0.6573 (4)	0.0569 (3)	0.0510 (8)
H3A	0.0992	0.7108	0.0147	0.061*
O1	0.7532 (3)	0.9739 (3)	0.14420 (15)	0.0384 (5)
O2	0.4950 (4)	1.0755 (3)	0.25118 (18)	0.0553 (6)

C4	0.6746 (5)	0.9881 (4)	0.2347 (2)	0.0336 (6)
C5	0.8110 (5)	0.8918 (4)	0.3301 (2)	0.0343 (6)
C6	1.0191 (5)	0.7974 (4)	0.3212 (2)	0.0398 (7)
H6A	1.0781	0.7893	0.2544	0.048*
C7	1.1397 (5)	0.7150 (4)	0.4110 (2)	0.0451 (7)
H7A	1.2798	0.6518	0.4054	0.054*
C8	1.0480 (5)	0.7285 (4)	0.5088 (2)	0.0421 (7)
C9	0.8406 (6)	0.8178 (5)	0.5205 (3)	0.0581 (10)
H9A	0.7807	0.8235	0.5875	0.070*
C10	0.7234 (6)	0.8990 (5)	0.4301 (3)	0.0568 (9)
H10A	0.5821	0.9601	0.4365	0.068*
N3	1.1799 (5)	0.6471 (4)	0.6046 (2)	0.0548 (7)
O3	1.3619 (6)	0.5690 (5)	0.5945 (3)	0.1018 (13)
O4	1.1007 (6)	0.6639 (5)	0.6907 (2)	0.0890 (10)
O5	0.1847 (3)	1.1006 (3)	0.09734 (16)	0.0385 (5)
H5A	0.252 (5)	1.088 (4)	0.1559 (14)	0.046*
H5B	0.069 (4)	1.043 (4)	0.112 (2)	0.046*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd	0.03111 (16)	0.02902 (15)	0.02818 (15)	−0.00363 (11)	−0.00305 (10)	0.00151 (10)
N1	0.0371 (12)	0.0309 (11)	0.0343 (12)	−0.0032 (10)	−0.0033 (10)	0.0009 (9)
C1	0.0417 (17)	0.0403 (16)	0.060 (2)	−0.0052 (14)	−0.0155 (15)	0.0081 (14)
C2	0.057 (2)	0.0329 (15)	0.063 (2)	−0.0156 (15)	−0.0132 (17)	0.0023 (14)
N2	0.0605 (17)	0.0342 (13)	0.0488 (16)	−0.0008 (13)	−0.0064 (13)	0.0059 (11)
C3	0.0523 (19)	0.0360 (15)	0.061 (2)	−0.0116 (15)	−0.0226 (16)	0.0051 (14)
O1	0.0343 (10)	0.0508 (12)	0.0283 (10)	−0.0078 (9)	−0.0042 (8)	−0.0022 (8)
O2	0.0432 (12)	0.0741 (16)	0.0449 (13)	0.0183 (12)	−0.0127 (10)	−0.0115 (11)
C4	0.0287 (13)	0.0375 (14)	0.0339 (14)	−0.0045 (12)	−0.0064 (11)	−0.0045 (11)
C5	0.0330 (14)	0.0394 (14)	0.0291 (14)	−0.0040 (12)	−0.0038 (11)	−0.0031 (11)
C6	0.0398 (15)	0.0456 (16)	0.0306 (14)	0.0047 (13)	−0.0003 (12)	−0.0034 (12)
C7	0.0398 (16)	0.0488 (17)	0.0413 (17)	0.0117 (14)	−0.0032 (13)	−0.0023 (13)
C8	0.0430 (16)	0.0457 (16)	0.0331 (15)	−0.0038 (14)	−0.0107 (12)	0.0036 (12)
C9	0.052 (2)	0.090 (3)	0.0283 (16)	0.0104 (19)	0.0000 (14)	−0.0078 (16)
C10	0.0446 (18)	0.087 (3)	0.0346 (17)	0.0216 (18)	−0.0033 (14)	−0.0120 (16)
N3	0.0543 (18)	0.0620 (18)	0.0407 (16)	−0.0015 (15)	−0.0138 (13)	0.0067 (13)
O3	0.079 (2)	0.147 (3)	0.0583 (19)	0.052 (2)	−0.0207 (16)	0.0044 (19)
O4	0.090 (2)	0.131 (3)	0.0339 (15)	0.017 (2)	−0.0135 (14)	0.0035 (16)
O5	0.0283 (10)	0.0424 (11)	0.0415 (12)	−0.0039 (9)	−0.0024 (8)	−0.0005 (9)

Geometric parameters (\AA , $^\circ$)

Cd—N1 ⁱ	2.254 (2)	C4—C5	1.513 (4)
Cd—N1	2.254 (2)	C5—C10	1.383 (4)
Cd—O1 ⁱ	2.364 (2)	C5—C6	1.385 (4)
Cd—O1	2.364 (2)	C6—C7	1.383 (4)
Cd—O5 ⁱ	2.370 (2)	C6—H6A	0.9300
Cd—O5	2.370 (2)	C7—C8	1.375 (4)
N1—C1	1.308 (4)	C7—H7A	0.9300

N1—C3	1.351 (4)	C8—C9	1.369 (5)
C1—N2	1.330 (4)	C8—N3	1.471 (4)
C1—H1A	0.9300	C9—C10	1.377 (5)
C2—N2	1.343 (4)	C9—H9A	0.9300
C2—C3	1.345 (4)	C10—H10A	0.9300
C2—H2A	0.9300	N3—O3	1.199 (4)
C3—H3A	0.9300	N3—O4	1.218 (4)
O1—C4	1.263 (3)	O5—H5A	0.842 (10)
O2—C4	1.245 (4)	O5—H5B	0.842 (10)
Cg1...Cg1 ⁱⁱ	3.6549 (2)		
N1 ⁱ —Cd—N1	180.0	C4—O1—Cd	120.39 (17)
N1 ⁱ —Cd—O1 ⁱ	86.19 (8)	O2—C4—O1	125.1 (3)
N1—Cd—O1 ⁱ	93.81 (8)	O2—C4—C5	117.7 (3)
N1 ⁱ —Cd—O1	93.81 (8)	O1—C4—C5	117.2 (2)
N1—Cd—O1	86.19 (8)	C10—C5—C6	118.9 (3)
O1 ⁱ —Cd—O1	180.0	C10—C5—C4	118.3 (3)
N1 ⁱ —Cd—O5 ⁱ	88.39 (8)	C6—C5—C4	122.8 (3)
N1—Cd—O5 ⁱ	91.61 (8)	C7—C6—C5	120.5 (3)
O1 ⁱ —Cd—O5 ⁱ	91.85 (7)	C7—C6—H6A	119.8
O1—Cd—O5 ⁱ	88.15 (7)	C5—C6—H6A	119.8
N1 ⁱ —Cd—O5	91.61 (8)	C8—C7—C6	118.5 (3)
N1—Cd—O5	88.39 (8)	C8—C7—H7A	120.7
O1 ⁱ —Cd—O5	88.15 (7)	C6—C7—H7A	120.7
O1—Cd—O5	91.85 (7)	C9—C8—C7	122.5 (3)
O5 ⁱ —Cd—O5	180.0	C9—C8—N3	118.7 (3)
C1—N1—C3	105.2 (2)	C7—C8—N3	118.8 (3)
C1—N1—Cd	128.3 (2)	C8—C9—C10	118.0 (3)
C3—N1—Cd	126.52 (19)	C8—C9—H9A	121.0
N1—C1—N2	111.8 (3)	C10—C9—H9A	121.0
N1—C1—H1A	124.1	C9—C10—C5	121.5 (3)
N2—C1—H1A	124.1	C9—C10—H10A	119.2
N2—C2—C3	106.7 (3)	C5—C10—H10A	119.2
N2—C2—H2A	126.6	O3—N3—O4	122.8 (3)
C3—C2—H2A	126.6	O3—N3—C8	118.8 (3)
C1—N2—C2	106.7 (3)	O4—N3—C8	118.4 (3)
C2—C3—N1	109.6 (3)	Cd—O5—H5A	98 (2)
C2—C3—H3A	125.2	Cd—O5—H5B	120 (2)
N1—C3—H3A	125.2	H5A—O5—H5B	104 (2)

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $-x+1, -y+1, -z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A \cdots O2	0.84 (1)	1.88 (1)	2.679 (1)	159
O5—H5B \cdots O1 ⁱⁱⁱ	0.84 (1)	1.97 (1)	2.785 (1)	164
C2—H2A \cdots O5 ^{iv}	0.93	2.58	3.244 (1)	129

C3—H3A···O5 ^v	0.93	2.43	3.344 (1)	169
C10—H10A···O2	0.93	2.42	2.751 (4)	101

Symmetry codes: (iii) $x-1, y, z$; (iv) $x, y-1, z$; (v) $-x, -y+2, -z$.